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NEUTRAL LIQUID CLEANING AGENT (I)
[NEUTRALES FLÜSSIGES REINIGUNGSMITTEL (I)]

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NEUTRAL LIQUID CLEANING AGENTS (I) /1*

The invention described in the following is in the area of aqueous cleaning agents that are planned for use in the household and commercially.

Currently aqueous surfactant solutions that may contain other active ingredients and additives are by far the majority used for cleaning objects of all types. For example, liquid all-purpose cleaners have found wide distribution in the household and commercially, with which surfaces of metal, painted wood, plastic, ceramic products and glass can be cleaned without problems. These cleaning agents, which usually contain anionic or non-ionic surfactants as important active ingredients can be used both in concentrated form and also in more or less diluted form. In addition, liquid cleaning agents are also used for cleaning textiles, especially textile floor coverings. In this case, use preferably occurs in diluted form or in the form of foam.

While earlier liquid cleaning agents usually had a strongly alkaline pH value, which promoted loosening of dirt, or else a relatively strong pH value if lime deposits were to be dissolved, in recent times a trend toward neutral cleaning agents has developed, which promise greater material protection and special skin compatibility. Reference is made here to, e.g., the German OLS 22 20 540 and the American patents 3 463 735, 3 882 038 and 3 939 090. Previously these advantages of the neutral cleaning agents generally

*Numbers in the margin indicate pagination in the foreign text.

had to be acquired at the price of certain disadvantages, of which only the lower cleaning power and the lower wetting capacity in comparison to the alkaline agents will be named.

In this context, the object of the present invention is to develop a neutral liquid cleaning agent that is improved in /2 comparison to the state of the art. In connection with the present invention, the neutral range is considered to be the range between the pH values 5 and 9, and especially between 6 and 8.

The solution according to the invention consists of an aqueous cleaning agent, which has a pH value in the above-mentioned range in undiluted state and is characterized in that it contains 1 to 25 weight-% of surfactant from the classes of non-ionic and/or synthetic anionic surfactants and 0.1 to 12 weight-% of alcohol from the group including benzyl alcohol, 2-phenoxyethanol, 2-phenylethanol and mixtures of them. This type of cleaning agent is especially preferred in which the content of these alcohols is 1 to 5 weight-%.

The cleaning agent according to the invention is characterized above all in that when used on hard surfaces it does not run together during drying to form drops and larger spots, but dries uniformly and leaves practically no visually disturbing residues on the surfaces. Simultaneously, the agents have extraordinarily high cleaning power both in undiluted and in diluted state. Besides that, it was found that the agents according to the invention can be stored even at unusually low temperatures without the appearances of separation occurring and without the need for special anti-freeze agents to be

added. Thus the agents represent a definite improvement overall in comparison to the state of the art.

Above all, the synthetic anionic surfactants that can be included in the agents according to the invention involve those of the sulfonate and sulfate types. Akylbenzene sulfonates with a C_9-C_{14} alkyl radical and olefin sulfonates, i.e., mixtures of alkene and hydroxyalkane sulfonates, like disulfonates as are obtained, e.g. from C_{12}-C_{18} monoolefins with double bonds located at end or on the inside, by sulfonating with gaseous sulfur trioxide and subsequent alkaline or acid hydrolysis of the sulfonating products, can be considered. Also suitable are the alkane sulfonates that can be obtained from C_{12}-C_{18} /3 alkanes by sulfochlorination or sulfoxidation and subsequent hydrolysis and/or neutralization by bisulfite addition to olefins, and the esters of α-sulfofatty acids, e.g., the α-sulfonated methyl or ethyl ester of hydrated cocoa, palm kernel or tallow fatty acids.

Suitable surfactants of the sulfate type are the sulfuric acid monoesters of long-chain primary alcohols of natural or synthetic origin, i.e., of fatty alcohols, e.g., coconut fatty alcohols, oleyl alcohol, lauryl, myristyl, palmityl or stearyl alcohol, or the C_{10}-C_{20} oxoalcohols or secondary alcohols with this chain length. The sulfuric acid monoesters of the aliphatic long-chain primary alcohols ethoxylated with 1 to 6 mol ethylene oxide (EO) and/or ethoxylated secondary alcohols are suitable. Besides that, sulfated fatty acid alkanolamides, sulfated fatty acid monoglycerides, long-chain sulfosuccinic acid ester and the salts of long-chain ether carboxylic

acids, which can be obtained, e.g., by reaction of long-chain alcohols ethoxylated with 1 - 10 mol EO with chloroacetic acid. The anionic surfactants are preferably used as alkali salts or the salts of alkanolamines with 2 to 6 C-atoms. Especially preferred anionic surfactants in the scope of the invention are the alkane sulfonates, the olefinic sulfonates and the fatty alcohol sulfates.

The synthetic anionic surfactants are contained in concentrations of up to 25 weight-% in the agents according to the invention. Preferably at least 1 weight-% is included. Agents that are provided for the undiluted use preferably contain 1 to 5 weight-% of the anionic surfactants, while agents that are preferable or exclusively used in diluted state usually contain larger quantities of these surfactants, preferably 1 to 11 weight-%.

Mainly the addition products of 3 to 20 mol ethylene oxide (EO) to primary C_{10}-C_{20} alcohols, e.g., to coconut or tallow fatty alcohols, to oleyl alcohol, to oxoalcohols of secondary alcohols of this chain length, are primarily suitable as non-ionic surfactants. In this case, in addition to the non-ionic water-soluble surfactants included here, /4 the not completely water soluble low ethoxylated fatty alcohol polyglycol ethers with 3 to 7 ethylene glycol ether radicals in the molecule are of interest, above all if they are used together with water soluble non-ionic or anionic surfactants. Also suitable are the corresponding ethoxylation products of other long-chain compounds, e.g., of the fatty acids and the fatty acid amides with 12 to 18 C atoms and the alkyl phenols with 8 to 16 C atoms in the alkyl section.

In all these products, instead of a part of the ethylene oxide, propylene oxide (PO) can also be added. Other suitable non-ionic surfactants are also the water soluble addition products containing 20 to 250 ethylene glycol ether groups and 10 to 100 propylene glycol ether groups of ethylene oxide to polypropylene glycol, alkylene diamino propylene glycol and alkyl polypropylene glycol with 1 to 10 carbon atoms in the alkyl chain, in which the polypropylene glycol chain functions as a hydrophobic radical. Mono and diethanolamides of the fatty acids are also suitable as non-ionic surfactants, for example the compounds N-coconut-alkyl-N,N-dimethylamine oxide, N-tallow-alkyl-N,N-dihydroxy ethylamine oxide, and also the water-soluble alkyl glycosides, the hydrophobic C_8-C_{20} alkyl radical of which is glycosidically linked with a usually oligomeric hydrophilic glycoside radical, e.g. C_{12}-C_{14} fatty alcohol + 1,6 glucose. In the agents according to the invention, ethoxylates of fatty alcohols or oxoalcohols with 5 to 15 mol EO, fatty acid ethanolamide and alkyl polyglucoside are preferred as non-ionic surfactants.

The non-ionic surfactants can be used in the agents according to the invention in quantities of up to 25 weight-%, with the criterion that the total of anionic and non-ionic surfactants make up 1 to 25 weight-% in the agents. In the agents that are used undiluted, the content of nonionic surfactants preferably lies between 1 and 5 weight-%, while in the agents that are preferably or exclusively used in diluted state, the content of these surfactants is higher and preferably 1 to 15 weight-%. In many cases, a mixture of anionic and

non-ionic surfactants is used since in this case synergies result, especially with respect to the cleaning effect. In these cases, a weight ratio of anionic to non-ionic surfactant like 7:1 to 1:1, and especially 5:1 to 2:1, is preferred. /5

In addition to synthetic anionic and/or non-ionic surfactants, the agents according to the invention can also contain amphoteric surfactants and especially soaps in larger quantity, if this is desired. The amphoteric surfactants involve long-chain compounds, the hydrophilic part of which consists of a cationically charged center (usually a tertiary amino or quaternary ammonium group) or an anionically charged center (usually a caboxylate or a sulfonate group). Examples of this type of surfactants are N-coconut-alkyl-N,N-dimethylamino acetate and N-dodecyl-N,N-dimethyl-3-amino propane sulfonate. The soaps involve alkali or ammonium salts of the fatty acids with 12 to 18 C atoms in the chain. Examples include C_{10}-C_{18} coconut fatty acid sodium salt, C_{16}-C_{18} tallow alkylammonium salt and myristinic acid potassium salt.

The content of amphoteric surfactants and/or soaps depends on the desired effect and with the amphoteric surfactants can be up to 10 weight-% and with the soaps up to 25 weight-%, related to the total agent. If these surfactants are contained in the agents, their concentration is 0.1 weight-%, and preferably 0.3 weight-%, while the upper limits preferably lie at 5 to 15 weight-%. High soap contents are especially provided in those agents, which, e.g., are to leave a protective matte gloss soap film behind when they are used on floor

coverings and that are therefore also designated as washing and care agents. High contents of amphoteric surfactants and/or soaps generally mean a lower content of anionic and/or non-ionic surfactants at the same time, so the total content of surfactants in the concentrated agents to be used in a diluted solution preferably does not lie over 15 weight-% and especially not over 10 weight-%.

Another important component of the agents according to the invention is the aromatic alcohols from the group benzyl alcohol, 2-phenoxyethanol and 2-phenylethanol that are contained individually or in a mixture in the agents. These alcohols are apparently responsible /6 for the special effects of the neutral cleaning agents according to the invention, in interaction with the anionic and/or non-ionic surfactants. It is notable that relatively low quantities of these alcohols are sufficient for the effects described. About 0.1 weight-% can be seen as a minimum content; preferably the agents contain no more than 12 weight-%. An especially preferred range lies between 1 and 5 weight-%, related to the total aqueous agent.

In addition to the constituents already named, the agents according to the invention can contain other active ingredients and additives, especially salts with cleaning actions, solvents, viscosity regulators, solutizers, colorants, preservatives and perfume oils, as long as these have no negative effects on the agent according to the invention.

The salts with cleaning action, which can be used in the agents in quantities of up to 10 weight-% involve water soluble salts,

especially alkali salts, of inorganic or organic acids that are used to improve the cleaning effect and the material compatibility and if necessary to suppress the influences of hard water. Sodium citrate, sodium triphosphate, monopotassium phosphate, potassium pyrophosphate, potassium carbonate and sodium hydrogen carbonate can be named as examples.

The solvents, which can be contained in quantities up to 10 weight-% in addition to the above-mentioned aromatic alcohols, involve completely water-miscible solvents from the group of alcohols with 2 to 4 C atoms and the lower ether alcohols with up to 8 C atoms, e.g., ethanol, isopropanol and ethane diol. These solvents also serve, in addition to other solutizers that may be used, to give the agent according to the invention a single phase, even if active ingredients that are not very water soluble are used. The solutizers, which are also called hydrotropics, usually involve salts of sulfonic acids that do not have a surfactant action, for example sodium xylene sulfonate, or compounds that greatly influence the structure of the water, e.g. /7 urea.

In the simplest case, the manufacturing of the agents can occur by mixing together all the components in any sequence. If active ingredients that are not very soluble in water are incorporated, it is frequently recommended that these first be mixed with the solutizers and then added to the aqueous solution of surfactants. The presence of the aromatic alcohols acts advantageously on the stabilizing of compounds that are not very soluble in water in the agents. If

necessary, the pH value is adjusted to the desired value in the neutral range (pH 5 to pH 9).

The agents according to the invention can be used both undiluted and also after greater or lesser dilution with water. In this case, one and the same agent can be used in undiluted state for removing heavy soiling, mostly in spot cleaning, as well as in diluted state for surface cleaning. However, generally agents that are intended completely for undiluted use are less concentrated than those agents for which a diluting step with water is regularly planned before actual use. Therefore, agents for undiluted use generally contain more than 80 weight-%, and preferably more than 90 weight-%, water while the agents that will be diluted can also have water contents below 30 weight-%, depending on the planned degree of dilution. Preferably their water content lies between about 40 weight-% and about 80 weight-%, depending on the intended degree of dilution, which can preferably be 1:3 to 1:500 and especially 1:5 to 1:50.

The actual cleaning process then consists in that an absorbent object, e.g., a cloth or a sponge, is impregnated with the cleaning agent, which may be diluted, and the surface to be treated is uniformly wiped with it. During this procedure, the soil is loosened from the surface and absorbed by the cloth and/or sponge, in order to then be released into the water or diluted cleaning agent solution when the cloth or sponge is rinsed with this medium. Since the agents dry extremely uniformly and streak-free on almost all surfaces, /8 generally a repeat rinsing with water and other post-treatments, like

polishing, can be dispensed with. While the diluted cleaning agent solutions can possibly also be used for cleaning textile floor coverings, for example with the spray extraction process, the focus of the application is on use for cleaning hard surfaces like floors, plastic surfaces, painted wood, glass panes and tiles.

Examples /9

Soap cleaner

The soap cleaners according to Examples 1 to 4 are produced by mixing the components indicated in Table 1. Unless otherwise indicated, the numbers in these and later tables represent weight percents, related to the finished agent and are always calculated as pure active substance.

The agents 2 to 4 were then compared to the agent 1 according to the invention with respect to their cleaning power and their cold stability.

The cleaning effect was determined with the use of a Gardner washability and abrasion testing device, as is described in the quality standards for washing and care agents of the Industrieverbandes Putz- und Pflegemittel e.V. [Cleaning and Care Agents Industrial Association] (Soaps, oils, greases, waxes, 108, pages 526-528 (1982)). In this method, a white PVC film is provided with test soil consisting of soot and grease and is washed mechanically under standardized conditions with a cloth soaked in diluted (1:500) cleaning agent solution. The cleaning performance is measured using photoelectric determination of the degree of remission.

To evaluate the cold stability, the samples are aged at 0 - 3°C for 12 weeks. During this time, the samples were taken out of the freezer weekly and after reaching room temperature, they were evaluated visually. Visible signs of instability were flocculation, sediment, suspensions and change in viscosity. The evaluation was made according to the following scale:

0 uniform, homogeneous sample

1 slight suspensions or sediment after 12 weeks

2 slight suspensions or sediment after 3 weeks

3 medium suspensions or sediment after 3 weeks

4 strong suspensions or sediment after 3 weeks

5 very strong suspensions or sediment after 3 weeks

Table 1 /10

Examples	1	2	3	4
Monochloracetamide	0.1	-	-	-
KOH	2.5	2.5	2.5	2.5
$C_{16/18}$ alkane sulfonate Na	13.5	13.5	13.5	13.5
Coconut alcohol + 5 EO + 4 PO	14.0	14.0	14.0	14.0
Coconut-palm kernel fatty acid	10.0	10.0	10.0	10.0
Ethanol	4.0	4.0	4.0	4.0
Perfume	0.5	0.5	0.5	0.5
2-Phenoxyethanol	-	2.0	-	-
2-Phenylethanol	-	-	-	1.5
Benzyl alcohol	-	-	2.0	-
Water	to make 100	to make 100	to make 100	to make 100
pH Value	8.5	8.7	8.7	8.7
Storage stability at 0 - 3°C	3	0	0	0
Remission values acc. to Gardner 0.2%	37	42	42	41

The advantages of the agent according to the invention are clear from the test results both in cold stability as well as in cleaning

effect.

Cleaner based on non-ionic surfactant

The components indicated in Table 2 are produced by intensive mixing of cleaners 5 to 8. In all cases, the perfume is mixed in as the last component. The agents 6 to 8 according to the invention are compared to the agent 5, which is not according to the invention, with respect to residue behavior during the cleaning of hard surfaces and with respect to incorporation of the perfume oil that is stable during storage. /11

The residue behavior of the agents was tested, in that 100 ml each of a 1% solution of the agent was allowed to run onto a black tile wall and dry. After complete drying, the residue is evaluated visually using a rating scale of -5 to 0:

-5 very strong streaking, cannot be polished

-4 strong streaking, difficult to polish

-3 medium-strong streaking, difficult to polish

-2 streak formation, can be polished

-1 slight streaking, easy to polish

0 no streaks or negative influence on gloss.

The stability of the perfume in the agents was tested in an aging test in alternating climate (12 hours at 0°C, 12 hours at 40°C). The evaluation was also visual in this case, according to the following scale:

1. Very good dispersion capability; the perfume oil drops are uniformly distributed in the solution and do not separate, even during

the aging test.

2. Good dispersion capability; only a part of the perfume separates and only as droplets at the end of the aging test.

3. Medium dispersion capability; a part of the perfume drops already separate after 4 weeks aging duration.

4. Poor dispersion capability; all of the perfume separates already after 4 weeks aging duration.

Table 2 /12

Examples	5	6	7	8
Monochloracetamide	0.1	-	-	-
Coconut alcohol + 10 EO butyl ether	10.0	10.0	10.0	10.0
Coconut fatty acid C_{12}-C_{18}	0.4	0.4	0.4	0.4
KOH	0.05	0.05	0.05	0.05
Benzene sulfonate -Na	0.8	0.8	0.8	0.8
Perfume	0.3	0.3	0.3	0.3
2-Phenoxyethanol	-	2.0	-	-
2-Phenylethanol	-	-	-	1.0
Benzyl alcohol	-	-	1.0	-
Water	to make 100	to make 100	to make 100	to make 100
pH Value	7.5	7.6	7.6	7.6
Residue behavior	-4	-1	-1	-1
Storage stability	4	1	1	1

The advantages of the agents 6 to 8 according to the invention in comparison to agent 5, which is not according to the invention, are clear from the testing results.

Cleaners based on anionic surfactant

Cleaners of this type (9 - 12) were produced by intensive mixing of the raw materials listed in Table 3. In all cases, the perfume was the last thing added to the mixture. Testing of the agents occurred according to the same criteria and with the same methods as in Examples 5 to 8.

Table 3 /13

Examples	9	10	11	11
Monochloracetamide	0.1	-	-	-
Citric acid	0.20	0.20	0.20	0.20
Sodium lauryl sulfate	2.50	2.50	2.50	2.50
Coconut fatty acid diethanolamide	1.00	1.00	1.00	1.00
Colorant	0.001	0.001	0.001	0.001
Perfume	0.5	0.5	0.5	0.5
2-Phenoxyethanol	-	1.0	-	-
2-Phenylethanol	-	-	-	0.75
Benzyl alcohol	-	-	1.0	-
Water	to make 100	to make 100	to make 100	to make 100
pH Value	7.0	7.0	7.0	7.0
Residue behavior	-3	0	0	0
Storage stability	4	1	1	1

The advantages of the agents 10 to 12 according to the invention in comparison to agent 9, which is not according to the invention, are clear from the testing results.

Patent Claims /14

1. Aqueous cleaning agent that has a pH value in the range from 5 to 9 in undiluted state and that contains 1 to 25 weight-% surfactant from the classes of non-ionic and synthetic anionic surfactants and 0.1 to 12 weight-% of alcohol from the group benzyl alcohol, 2-phenoxyethanol, 2-phenylethanol and mixtures of them.

2. Cleaning agents according to Claim 1, containing 1 to 5 weight-% of alcohol from the group benzyl alcohol, 2-phenoxyethanol, 2-phenylethanol and mixtures of them.

3. Cleaning agents according to one of Claims 1 or 2, which have a pH value between 6 and 8 in undiluted state.

4. Cleaning agents according to one of Claims 1 or 3, which contain 0.1 to 25 weight-% soap as another active ingredient.

5. Cleaning agents according to one of Claims 1 or 4, which contain 0.1 to 10 weight-% amphoteric surfactant as another active ingredient.

6. Cleaning agents according to one of Claims 1 or 5, which contains other auxiliary agents and additives from the group of salts with cleaning action, solvents, solutizers, colorants, perfume oils and mixtures of them.

7. Use of a cleaning agents according to one of Claims 1 or 6 in undiluted state for cleaning hard surfaces.

8. Use of a cleaning agents according to one of Claims 1 or 6 after dilution with water in a weight ration of 1:3 to 1:500, and preferably 1:5 to 1:50, for cleaning textile floor coverings or hard surfaces.